Highly efficient hydrogenation of cinnamaldehyde catalyzed by Pt-MCM-48 in supercritical carbon dioxide

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In supercritical carbon dioxide medium, a platinum-containing cubic mesoporous molecular sieve was shown to promote markedly the selective hydrogenation of *trans*-cinnamaldehyde, giving an excellent selectivity for cinnamyl alcohol. In contrast to the other platinum-containing conventional catalysts, Pt-MCM-48 can be recycled a number of times without showing any deactivation in the studied reaction condition. The selectivity mainly depends on the pressure of carbon dioxide, while the conversion depends on the pressure of carbon dioxide as well as hydrogen pressure.

KEYWORDS: *trans*-cinnamaldehyde; hydrogenation; Pt-MCM-48; supercritical carbon dioxide.

1. Introduction

Catalytic hydrogenation is a commercially important class of reaction, especially the hydrogenation of α,β-unsaturated carbonyl compounds to produce fine chemicals [1], normally carried out in liquid phase, organic solvent through homogeneous catalysis. The selective synthesis of α,β-unsaturated alcohol is very difficult to achieve, because it is known that the C=C bond hydrogenates more easily than the C=O bond and produces different side products. The large-scale use of liquid organic solvents has substantial environmental concerns, providing the current impetus for the development of alternative ecologically friendly reaction solvents. Supercritical carbon dioxide ($scCO_2$) has been considered as an attractive replacement for the conventional organic solvent due to its moderate critical parameter, environmentally benign nature, and potentially easy product separation. $scCO_2$ affords some potential advantages for the hydrogenation reaction, particularly the enhanced rate of mass transfer [2a], product selectivity [2b], improvement in catalyst's lifetime [2c], etc. Homogeneous catalysis has already been well studied in a supercritical solvent medium [3].

However, there are very few reports on heterogeneous catalysis [4,5]. Literature data reveal that in organic solvents, in the presence of heterogeneous catalysis, the selectivity to unsaturated alcohol can be governed by several factors such as the nature of the supports [6], presence of promoters like Sn and other metals [7], reaction media [8] and also Lewis acid centers on the support, which provide suitable anchoring sites for C=O moieties [6].

Among various catalysts, noble-metal-encapsulated zeolites have been considered as potential catalysts in regioselective hydrogenation reactions in which high selectivity toward unsaturated alcohol has been observed over a platinum cluster in zeolite Y [9]. But the disadvantages of using those catalysts are the slow reaction rate due to the immiscibility of hydrogen in the organic solvent as well as quick inactivation of the catalysts. Addition of promoters like $FeCl_2$ and $GeCl_4$ to the supported platinum catalysts was necessary to increase the selectivity of the reaction to the unsaturated alcohol, due to the presence of the electron-deficient centers on the catalyst surface [7].

The discovery of mesoporous materials has provided new possibilities in catalysis [10]. They have some unique characteristics such as large pores, high surface area, and controllable and narrowly distributed pore sizes that make them a very promising candidate as catalyst, catalyst support and adsorbent. In particular, the cubic structure of mesoporous MCM-48 material makes it more attractive for different catalytic applications because of its pore architecture. To develop a truly environment-friendly process, we have combined the advantages of mesoporous material as the heterogeneous catalyst and $scCO_2$ as the reaction medium. This ensured us a challenging task, focusing on chemo- and regioselective catalytic hydrogenation of α,β-unsaturated aldehyde compounds to selectively and efficiently produce α,β-unsaturated alcohols (scheme 1). To the best of our knowledge this is the first report of selective hydrogenation of cinnamaldehyde in $scCO_2$ medium using a mesoporous catalyst like Pt-MCM-48.

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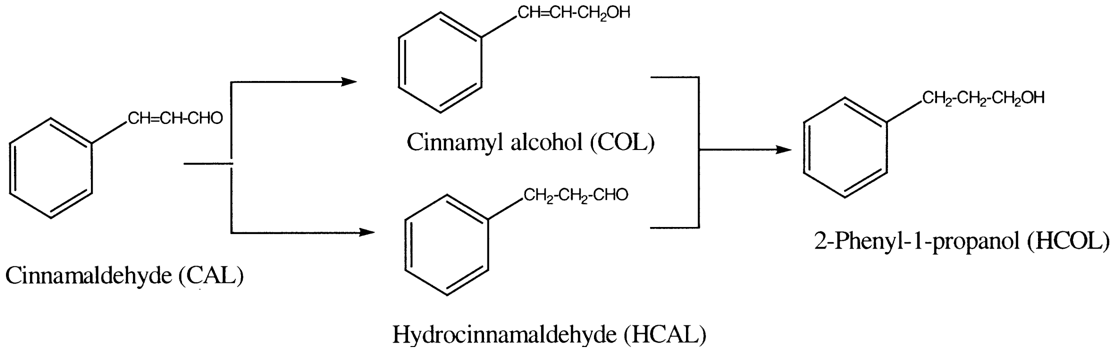

Scheme 1.

2. Experimental

The Pt-MCM-48 catalyst was prepared under hydrothermal conditions using chloroplatinic acid as the source of platinum from the gel with the following molar composition:

$$1\,SiO_2 : 0.61\,CTABr : 0.25\,Na_2O : x PtO : 61\,H_2O.$$

The detailed synthesis and characterization of the catalyst was described elsewhere [11]. This *in-situ* synthesis of Pt-MCM-48 was found to result in a good distribution of the platinum particle after calcination. The hydrogenation of cinnamaldehyde (CAL) was carried out in a stainless steel batch reactor using 100 mg of 1 wt% Pt-MCM-48 and 7.5 mmol of the reactant at 50 °C. A prescribed amount of hydrogen was first loaded into the reactor. Liquid CO_2 was charged into the reactor using a high-pressure liquid pump and then compressed to the desired pressure. The hydrogen and the reaction mixture were stirred continuously with a magnetic stirrer in $scCO_2$ during the reaction (for 2 h). A back-pressure regulator maintained a constant pressure in the system. The products were identified by GC/MS and analyzed quantitatively by GC (HP 6890, capillary column with flame ionization detector).

3. Results and discussion

According to the literature, the hydrogenation of CAL leads to the formation of hydrocinnamaldehyde (HCAL), cinnamyl alcohol (COL) and phenyl propanol (HCOL) in the presence of heterogeneous catalysts [12]. Table 1 presents the conversion and selectivity as a function of hydrogen pressure and pressure of $scCO_2$. Complete sets of results for the hydrogenation of CAL in $scCO_2$ and 1-propanol are also shown in table 1. Using Pt-MCM-48 catalyst in $scCO_2$ medium, under 4 MPa hydrogen pressure at 50 °C excellent selectivity of the formation of cinnamyl alcohol (96.6%) was obtained. An interesting and significant pressure dependence was observed (table 1) in which the selectivity to cinnamyl alcohol was increased with increasing pressure and reached a maximum, then decreased sharply (Runs 2–4). A quantitative consideration of this phenomenon may be explained by the higher compressibility of

Table 1
Hydrogenation of cinnamaldehyde

Run	Pressure (MPa)		Conversion (%)	Selectivity (%)		
	H_2	CO_2		COL	HCAL	HCOL
1	4.0	–	3.6	45.6	39.6	14.8
2	4.0	7.0	14.6	59.5	30.3	10.2
3	4.0	8.5	21.5	78.5	13.6	7.9
4	4.0	10.0	30.8	96.6	2.5	0.9
5	4.0	12.5	33.6	77.4	17.9	4.7
Effect of hydrogen pressure						
6	2.0	10.0	21.2	85.2	10.3	4.5
7	4.0	10.0	30.8	96.6	2.5	0.9
8	6.0	10.0	38.7	93.2	6.0	0.8
In 1-Propanol						
9	4.0	–	22.6	54.7	38.6	6.7

All the reactions were carried out at 50 °C, 7.5 mmol reactant, 100 mg catalyst (1% Pt), 2 h reaction time.

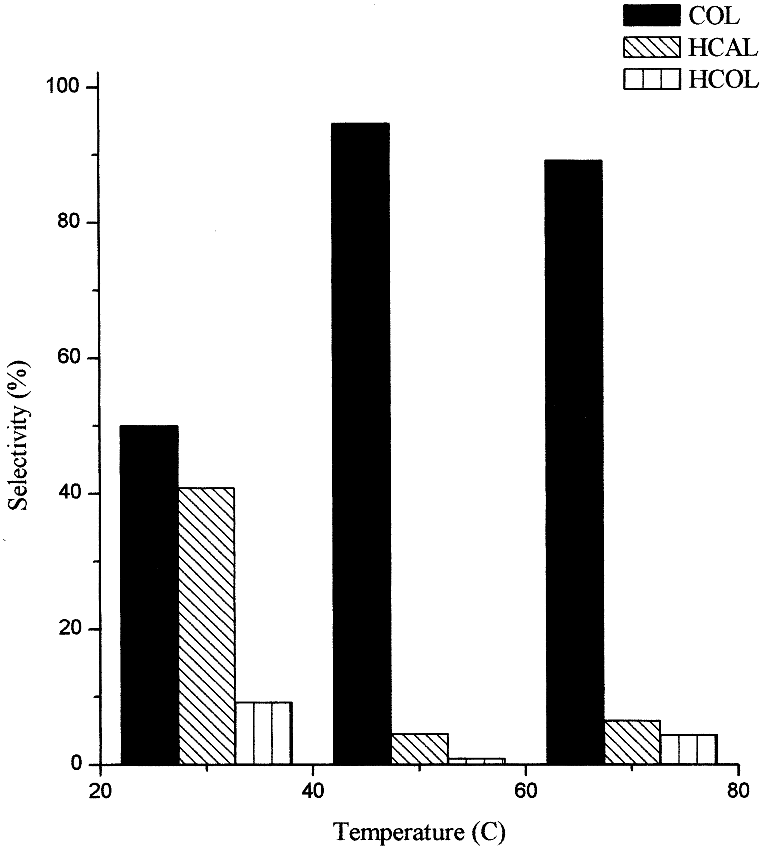

Figure 1.

$scCO_2$ around the critical point, which is responsible for the local dielectric constant being much larger than the bulk area, making the solvent more polar. This may affect the reactivity of C=O and hydrogenate the bond more easily [13] because of polarity. But at higher pressures, as the compressibility decreases, the local dielectric constant is very near the bulk value and that results in the lower selectivity.

To check the effect of $scCO_2$, the reaction was carried out in an atmosphere of hydrogen alone, under the same reaction condition (Run 1). The conversion drops sharply in the absence of $scCO_2$. As a consequence, one can explain the above result by considering the excellent miscibility of hydrogen in $scCO_2$. The hydrogen concentration at the catalyst surface can be greatly increased, leading to the enhancement of the rate of the reaction. Therefore, the effect of hydrogen pressure is an important factor regarding the hydrogenation reaction in $scCO_2$ medium. Hence, we have examined the effect of hydrogen pressure on the activity and selectivity for cinnamyl alcohol, and the results are given in table 1 (Runs 6–8). An enhancement in activity and selectivity were observed with increasing hydrogen pressure. The activity was increased with hydrogen pressure and reached 38.7% at 6 MPa of H_2 and 10 MPa of CO_2. It is important to note that the selectivity of COL is higher at 4 MPa of H_2 pressure. On the basis of this series of results, 4 MPa H_2 pressure was selected for the study of temperature dependence. The rate of the reaction also increases continuously, but selectivity passes through a maximum at 50 °C (figure 1). A smaller selectivity of 54.7% was obtained in 1-propanol under 4 MPa of hydrogen pressure (Run 9). In contrast to conventional catalysts, there is no indication of the formation of acetol, so the poisoning of Pt by the formation of CO can easily be ignored. The Pt-MCM-48 was recycled more than twice, showing no deactivation has occurred under the present reaction conditions.

4. Conclusion

In conclusion, we have developed a highly efficient recoverable, heterogeneous catalyst for selective hydrogenation of cinnamaldehyde in $scCO_2$. The use of a noble metal such as Pt-supported MCM-48 in $scCO_2$ medium can successfully enhance the selectivity of unsaturated alcohol, similar to that seen in liquid-phase catalysis. High selectivity combined with good reaction rate is a beneficial feature of this process. The use of $scCO_2$ medium makes it more convenient in the easy separation of the catalyst from the reactant/product and also permits us to incorporate this new catalyst in the field of green and clean chemistry.

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